TITLE:

Photopolymerization Induced Phase Transition in Polymer Dispersed Liquid Crystals and Photonic Crystals

AUTHOR(S):

Kyu, Thein

CITATION:

Kyu, Thein. Photopolymerization Induced Phase Transition in Polymer Dispersed Liquid Crystals and Photonic Crystals. 物性研究 2006, 87(1): 16-17

ISSUE DATE:

2006-10-20

URL:

http://hdl.handle.net/2433/110676

RIGHT:

京都大学学術情報リポジトリ
KURENAI 紅
Kyoto University Research Information Repository

Photopolymerization Induced Phase Transition in Polymer Dispersed Liquid Crystals and Photonic Crystals

Thein Kyu
Department of Polymer Engineering, University of Akron
Akron, OH 44325-0301

1. Introduction:

Photonic crystals are dielectric substances with periodic structures that are structured to exhibit photonic band gap characteristics,[1,2] where propagation of light is prohibited in a certain range of frequencies. Analogous to the electronic band gap counterpart, conventional photonic materials possess structures with a high dielectric constant contrast with air.[3]

Photonic band gap materials are fabricated by holographic lithography involving pattern photopolymerization. Photopolymerization induced phase transition is a phenomenon of non-equilibrium and non-linear phase transformation[1] involving liquid-liquid phase separation and mesophase ordering from isotropic liquid (or melt) driven by photochemical reaction[4-6]. Basically, holographic lithography technique operates based on the principles of multi-beam optical interference in creating 1-dimensional and multi-dimensional periodic interference patterns with alternating low intensity and high intensity regions. These photo-patterns are imprinted onto the mixtures of photo-curable monomers and liquid crystals to produce switchable photonic crystals. Although the dielectric contrast in the holographic polymer dispersed liquid crystals (H-PDLC) may be comparatively small, the electrical switchability makes such H-PDLC materials unique. The primary objective of the present study is directed to experimental and theoretical elucidation of the formation of polymer dispersed liquid crystals and photonic crystals induced by photo-patterning. Theoretical modeling and simulation was undertaken to guide the holographic and photonic fabrications.

2. Results and Discussion:

A hypothetical phase diagram of a starting mixture of nematic LC and photo-monomer was constructed by solving the combined free energies of Flory-Huggins theory of liquid-liquid demixing and Maier-Saupe theory for nematic ordering. The self-consistent solution reveals an upper critical solution temperature (UCST) overlapped with a nematic-isotropic transition gap of the LC constituent (Figure 1a) exhibiting various coexistence regions such as liquid-liquid bound by the UCST, liquid-nematic bound by the solidus and liquidus lines and pure nematic regions.

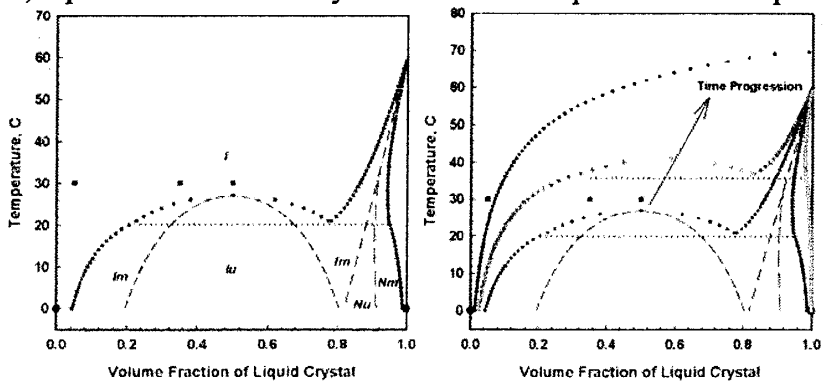

Figure 1. (a)A hypothetical phase diagram of monomer and nematic liquid crystal mixtures and (b) illustrations of phase diagram evolution with elapsed time during the photo-polymerization.

As guided by the phase diagram, the starting acrylate/LC mixtures in the single phase region were irradiated uniformly by UV. During photopolymerization, the average molecular weight of the reactive constituent increases which in turn makes the system to become unstable and eventually drives phase segregation in the polymer blends. Once the photo-polymerization

starts, monomers get polymerized and the upper critical solution temperature phase diagram of the starting mixture moves asymmetrically upward due to increasing molecular weight, thrusting the system from the initial stable state into the unstable region (Figure 1b).

In the hologram writing, the LC/monomer mixture is exposed to various interference laser beam configurations. Figure 2a represents the SEM micrograph of the 35/65 E7/penta-acrylate mixture reported by Bunning et al.[4] The submicron size-stratified pattern was obtained with a periodicity of a couple of hundreds nanometers and an average diameter of the individual droplet being 50 ~100 nm. A similar study has been extended to other compositions and also under various laser beam configurations to create 2D and 3D photonic crystals. It was found that the final morphologies are strongly dependent on the initial location of the system in the starting phase diagram.

The pattern forming aspects of photo-polymerization induced phase transition in mixtures of emerging polymer and nematic liquid crystal were modeled by means of the time-dependent Ginzburg Landau equations (TDGL, Model C) pertaining to a conserved compositional order parameter, and a non-conserved orientation order parameter coupled with photo-polymerization reaction kinetics. The spatio-temporal growth of the structure has been simulated on a 128×128 grid by employing a finite central difference method for the spatial step and an explicit forward difference method for the time step under a periodic boundary condition. The numerical solutions of these equations afford the dynamics of the H-PDLC structure formation. Figure 2b exhibits the simulated H-PDLC structures which revealed striking resemblance to the experimentally observed morphology.

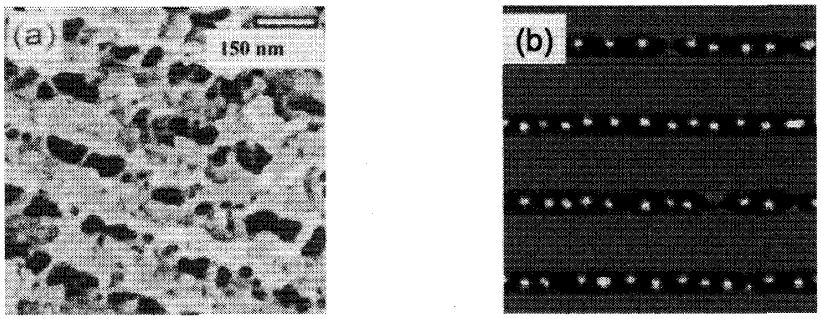

Figure 2: Comparison of (a) SEM morphology of pentacrylate based H-PDLC after extraction of LC with (b) the simulated one showing the LC domains in stratified layers.

The electrical switching characteristics of these H-PDLC films show the characteristic length to be comparable to the average sizes of the simulated liquid crystal domains. The striking similarity between the morphological patterns and the diffraction efficiency (DE) behavior of the theoretical calculation and the experiment is quite promising.

Acknowledgment: Support of this work by the National Science Foundation through grant number DMR 0514942 is gratefully acknowledged.

References:

1). E. Yablinovitch , Phys. Rev. Lett., **58**, (1987) 2059.

2). B. E. A. Saleh and M. C. Teich, "Fundamentals of Photonics," John Wiley & Sons: New York (1991).

3). H.M. Boots, J.G. Kloosterboer, G. Serbutoviez, and F.J. Touwslager, Macromolecules **29**, (1996)7683

4). T.J. Bunning, L.V. Natarajan, V.P. Tondiglia, R.L. Sutherland, D.L. Vezie, W.W. Adams, Polymer **36**, (1995) 2699

5).S. Meng, T. Kyu, L.V. Natarajan, V. P. Tondiglia, R.L. Sutherland, and T.J. Bunning, Macromolecules, **38**, (2005) 4844

6) T. Kyu, S. Meng, H. Duran, N. Kumar, and G. Yandek, Macromol. Res., **14**, (2006).155